Evaluating the Petroleum Vapor Intrusion Pathway

Studies of Natural Attenuation of Subsurface Petroleum Hydrocarbons & Recommended Screening Criteria

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by

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OBJECTIVE

- Understand why so many LUST sites exist nationwide, but few report cases of petroleum vapor intrusion to indoor air
- Develop guidance for screening/exclusion criteria to determine when PVI pathway is incomplete
- Avoid unnecessary, \$costly\$ PVI investigations

SCOPE

- Petroleum Vapor Database: *Compile basic, high-quality field data to evaluate vapor intrusion pathway:* soil type, source extent & degree, LNAPL, DTW, contaminant concentrations in dissolved & vapor phases
- Show mechanisms, characteristics & trends of petroleum hydrocarbon vapor biodegradation

The objective of studying and evaluating the behavior of subsurface petroleum vapors is to understand why, with so many LUST sites worldwide, the PVI pathway is rarely complete. Advancing our knowledge enables us to develop screening criteria to determine when PVI investigations are necessary.

The scope of evaluating the PVI pathway involves collecting and compiling basic site data (Petroleum Vapor Database). A LUST site must be fully characterized by collecting basic, good-quality data wherein the nature, extent & degree of contamination and contaminant sources are fully defined (required by 40 CFR Part 280) and provide knowledge of contaminant distribution in soil and groundwater, including temporal effects such as fluctuating DTW. Once these subsurface characteristics are understood, LUST PMs can better understand if the PVI pathway may be complete and if VI investigations are really necessary. VI investigations are costly and highly invasive to properties and their occupants, and unnecessary work should be avoided.

Detailed discussion of the Petroleum Vapor Database is provided in Davis R.V., 2009, LUSTLine #61.

Recent Timeline & History 2002-2010

Work Groups & Studies of Petroleum Hydrocarbon Vapor Intrusion



• 2002: EPA OSWER Draft Guide for Vapor Intrusion Evaluations:

- > Comprehensive
- Cautious screening criteria
- Recommends for chlorinated hydrocarbons, NOT petroleum LUST sites because biodegradation is not considered
- > Recommends forming work group to study VI pathway for petroleum
- 2003-2005: EPA OUST & States Petroleum Vapor Intrusion Work Group
 - Studied behavior of subsurface petroleum hydrocarbons associated with PVI pathway
 - > Compiled international database (U.S. & Canada)
- 2005-2010: Continued Field & Modeling Research Studies
 - EPA OUST PVI Work Group revived, database much larger, testing models, preparing to publish PVI guidance
 - American Petroleum Institute (API) Work Group, peer-reviews EPA OUST petroleum vapor database, compiles more data
 - Bio Vapor Model: Analytical Model, accounts for biodegradation of petroleum hydrocarbons in the subsurface (DeVaull and McHugh, 2010)

The EPA OSWER Draft Guide presents screening criteria for soil vapor and groundwater that are based in part on the Johnson & Ettinger Model (1991). The J&E Model is a good screening tool for halogenated (chlorinated) hydrocarbons that do not degrade easily. But because the Model does not account for biodegradation, it underestimates vapor attenuation of petroleum hydrocarbons by many orders of magnitude and thus overestimates risk of VI for petroleum hydrocarbons. The Draft Guide recognizes that the screening criteria are therefore overly conservative and recommends the guide not be used for petroleum hydrocarbon sites, and recommended forming a work group to study the behavior and fate of petroleum hydrocarbons.

The EPA OUST PVI Work Group was unfortunately discontinued in 2005 before recommendations could be made.

Numerous studies on PVI have been undertaken by many distinguished scientists and engineers. By 2007, API saw the great value in those studies and the work by the EPA OUST Work Group and formed its own work group (API Petroleum VI Work Group). The API Work Group peer-reviewed my Petroleum VI d-base and compiled about 4600 more vapor sample events, mostly from Colorado's impressive d-base of their LUST case files. The API d-base is stored in MS Access where multiple parameters can be simultaneously compared. The API Work Group discovered that, with such a large database, not all parameter comparisons return meaningful results regarding vapor attenuation because anomalies cannot be characterized without a subjective, qualitative analysis of the data in case files. Therefore, the Petroleum VI d-base is kept separate from the API d-base to provide an additional tool for evaluating data more subjectively.

The EPA OUST PVI Work Group re-formed in 2009, and the Petroleum Vapor Database is very large.



The characteristics of subsurface petroleum vapor attenuation and causes of vapor intrusion by petroleum hydrocarbons are well-understood. For vapors to biodegrade and attenuate, there must be a sufficient thickness of clean, aerobic soil that contains oxygen between 1% (DeVaull, 2007) and 6% (Davis R.V., 2009; Sanders and Hers, 2006).

There are no reported cases of vapor intrusion from low dissolved source strengths. All reported cases of vapor intrusion from petroleum sources are caused by LNAPL/free product, contaminated soil or very high dissolved concentrations in direct contact or proximity to buildings or anthropogenic/engineered preferential pathways such as sumps, elevator shafts, improperly sealed utility conduits into buildings, and groundwater cleanup systems (i.e. air sparging) that do not adequately capture vapors.



Build a Site Conceptual Model based on site-specific data. Title 40 of the Code of Federal Regulations, Part 280 for leaking USTs requires that sites be fully characterized, and decisions be based on adequate site characterization where the extent and degree of contamination and contaminant sources are known and well-defined. The presence and thickness of clean soil above contaminant sources are generally known in the early phases of site characterization. Clean soil contains the necessary oxygen for biodegrading PHCs and can be easily characterized with accurate logs of soil cores and samples.

Volatile compounds associated with LNAPL, contaminated soil, and very high dissolved contaminant concentrations can generate very high vapor concentrations that, when in close proximity to buildings or utilities, can cause PVI. Those conditions are the only known cases of petroleum vapor intrusion.

Contaminants dissolved in GW partition to vapor phase according to Henry's Law Constant. There are no known or reported cases of petroleum vapor intrusion associated with low dissolved-phase concentrations at or near buildings or utilities.



Profile of a typical vapor monitoring well from Petroleum Vapor d-base shows unmistakable signature characteristics of subsurface vapor attenuation: Each symbol represents depth of a vapor completion point in a multi-depth vapor monitoring well. Contaminants near source exhibit high vapor concentrations, with associated oxygen depletion & carbon dioxide enrichment. As contaminant vapors diffuse upward through clean, oxygenated soil, they degrade aerobically wherein oxygen is consumed, carbon dioxide is produced, and contaminant concentrations decrease away from source. When contaminants are degraded, oxygen and carbon dioxide rebound to near-atmospheric concentrations.



PHC vapors cannot attenuate because there is insufficient thickness of clean soil overlying the contaminated soil source. Without shallower vapor completion points, there is no way of knowing if vapors decrease and soil oxygen concentrations increase before reaching an overlying receptor.



This slide shows benzene and TPH vapor profiles of vapor well VW-11 from two different sampling dates, the earlier 8/06 event having no shallow completion. Vapor concentrations are very high within the contaminated soil zone (patterned area) and, from the 8/26/06 sampling event where the shallowest vapor sample was obtained from 4 feet deep, vapors appear to not attenuate below the overlying paved road. However, on 6/27/07, vapor samples obtained from 2.5 feet deep showed nearly complete vapor attenuation. Leak testing confirmed the good integrity of each completion point.

Some practitioners maintain that vapor completion points set too shallow (some say <5 feet deep) may be subject to short-circuiting or otherwise drawing in atmospheric air, causing a false-negative effect on vapor analyses. Others argue that this effect is not occurring at most sites because, according to standard sampling practices, vapor samples are obtained relatively quickly ("grab samples") and draw vapor in from the area directly around the completion point. Studies in Utah show that only faulty completion points or unnecessarily long sampling times result in drawing in atmospheric air. VW-11 is an example that shows the benefits of shallow completion points out-weighing the perception that short-circuiting might occur.



Magnitude of subsurface AFs is expressed by dividing the shallow soil vapor concentration by the deep soil vapor concentration. The lower the AF, the greater attenuation and contaminant reduction. Significant attenuation is observed when the petroleum contaminant source has 2 to 10 feet of clean overlying soil. This example shows that vapors associated with a very high source strength are fully attenuated with 7 to 8 feet of clean overlying soil and the AF is very low.



This map shows the number of geographic locations and soil vapor sample events (benzene) available for evaluating attenuation and developing screening criteria. Data are currently available from sites in Canada, United States and Australia. There are approximately equal numbers of geographic locations and soil vapor events for TPH measurements.

The Petroleum Vapor Database contains measurements for spatial and temporal subsurface soil vapor sample events from multi-depth and sub-slab vapor sample points, GW measurements, reports of LNAPL if present, soil boring logs, and soil data.

The Petroleum Vapor Database was originally constructed in 2003-2005 as part the EPA OUST PVI Work Group evaluation of vapor intrusion from petroleum-only sources. This originally small database is now much larger due to continued intensive and global investigation of the petroleum vapor intrusion pathway. There is now greater confidence in making meaningful interpretations of petroleum hydrocarbon contaminated sites and determining when the petroleum vapor intrusion pathway may be complete.



The Petroleum Vapor Intrusion d-base contains abundant data for subsurface SV events from which meaningful AFs are derived: benzene 237, TPH 189, including many sample events beneath buildings (benzene 53, TPH 41).

Results: Insignificant AFs >1E-02 (<100-fold contaminant reduction) are due to 3 Reasons: 1) No clean soil overlying the source; 2) Low source strengths; 3) Vapors attenuate directly above even very strong sources. Of the SV events exhibiting significant attenuation, the majority of shows \geq 10,000-fold reduction contaminant vapor concentration (AF \leq 1E-04).

The database contains many single-point sub-slab vapor events from which AFs cannot be determined but are still valuable for general, qualitative evaluation. Some of those sub-slab points have multi-depth vapor monitoring wells adjacent to the building ("near-slab" or "exterior"). The d-base has only one site where vapor intrusion is reported to occur: Stafford, New Jersey Building #73 (Sanders and Hers, 2006) because very high dissolved gasoline contaminant concentrations occur only 5 feet below the building. Benzene vapors do not intrude the building (dissolved benzene 12,000 ug/L) but MTBE, 2,2,4-Trimethylpentane and Cyclohexane do (dissolved MTBE 590,000 ug/L).

Adequate site characterization identifies these characteristics of attenuation and can determine the need for VI investigations.



BioVapor has been peer-reviewed by the EPA PVI Work Group.

From the BioVapor User's Manual:

"BioVapor is a user-friendly spreadsheet implementation of the Indoor Vapor Intrusion with Oxygen-Limited Biodegradation model presented in DeVaull, 2007. This algebraic model incorporates a steady-state vapor source, diffusion-dominated soil vapor transport in a homogeneous subsurface soil layer, and mixing within a building enclosure. The soil is divided into a shallow aerobic layer including firstorder biodegradation and a deeper anaerobic layer in which biodegradation is neglected. Model equations are provided in Appendix B of this guide. The user has three options for specifying the oxygen supply below the building foundation: 1) direct entry of the depth of the aerobic zone below the building foundation, 2) constant oxygen concentration below the building foundation, or 3) constant flow of atmospheric air below the building foundation. For Options 2 or 3, the model is solved by iteratively varying the aerobic depth to match oxygen demand (due to baseline soil respiration and biodegradation of chemicals) to oxygen supply. In the absence of aerobic biodegradation, the model is essentially equivalent to the Johnson and Ettinger (1991) vapor intrusion model. Although other analytical models have accounted for biodegradation with 1st-order decay, BioVapor improves on this method by accounting for limited oxygen availability."



Vapor profiles of field data compared to BioVapor Model using high-strength dissolved source (although LNAPL is likely) and three scenarios, each using the same AF and O2 and foc concentrations: 1) overlying bare earth (actual on-site condition); 2) overlying pavement, and; 3) specified depth of aerobic zone, which in this case is known from multi-depth SV points, and can also be determined from routine soil boring logs. The Model closely reflects the site conditions within less than 1 order of magnitude.



BioVapor Model run using benzene and TPH-gro subsurface soil vapor source concentrations. For benzene and TPH-g, the model run using defaults O2=1%, foc=0.5%, under-predicts attenuation by 100x to >1000x.

VW-7 is completed beneath asphalt about 5 feet away from building edge.



Dr. Lilian Abreu (Arcadis) developed a 3-D numerical model to simulate the behavior of volatile organic compounds, including petroleum hydrocarbons in the subsurface beneath buildings. The Model also simulates subsurface oxygen that naturally diffuses in from atmospheric air, mixes in the subsurface, and facilitates degradation of petroleum hydrocarbons.

Shown here are 3 Model runs simulating a building basement scenario with increasingly stronger vapor source strengths. As the vapors diffuse upward, they are attenuated as shown by the "iso-attenuation contours." The bottom panel shows the Model run using the strongest vapor source of 10,000,000 ug/m3, which generally represents LNAPL, and indicates vapors are attenuated with about 10 feet of overlying soil. These results accurately reflect field conditions observed in the Petroleum Vapor Database.

Conclusions from Models

BioVapor Model:

> Under-predicts subsurface attenuation & overpredicts PVI by 10xxxx for low-to-medium-high source strength

Very high-strength sources likely need PVI investigation

Abreu-Johnson Numerical Model:

Vapors associated with low source strengths beneath buildings are attenuated with a few feet of clean overlying soil

Developing Screening Criteria

Determine Thickness of Clean Overlying Soil Required to Attenuate Vapors Associated with:

Dissolved Sources

LNAPL & Soil Sources

Screening criteria are important for determining when vapor intrusion investigations are necessary. Data analysis of the Petroleum Vapor database shows that vapors attenuate with some amount of clean overlying soil, and those sites exhibiting significant vapor attenuation have subsurface AFs \leq 0.01 (i.e., high attenuation of contaminants by greater than or equal to 100-fold). These AFs are different from the BioVapor AF because subsurface AFs express attenuation due to biological processes and degradation of petroleum compounds in the vadose zone.

Many practitioners want to know how much clean overlying soil is required to fully attenuate vapors of a particular dissolved source strength. To understand this relationship, I evaluated the Petroleum VI d-base for sites in which the following characteristics are known: depth to GW, and depth, distribution and strength of contaminant sources and their associated vapors.

Finally, Project Managers must determine the need for sub-slab sampling because it is highly-invasive to building owners & occupants. This procedure has been met with understandable resistance in Utah and likely elsewhere.



The Petroleum Vapor d-base contains abundant high-quality data for benzene and TPH sample events that were evaluated line-by-line. These data include depth to groundwater, dissolved concentrations and proximal and concurrent multi-depth soil vapor concentrations.

<u>Method</u>: subtract depth of deepest clean vapor sample point from the depth to groundwater. In this case, it takes 8 feet of overlying soil to attenuated vapors associated with 16,000 ug/L benzene dissolved in GW. This method is conservative because it does not account for contaminated smear zone soils that may be present.

The Petroleum Vapor d-base contains enough high-quality data to determine thickness of clean overlying soil necessary to fully attenuate vapors from their respective dissolved source strengths. There are numerous paired benzene and TPH SV & GW field measurements from about 100 geographic locations. Conservative screening criteria emerge showing that vapors associated with dissolved benzene sources of about 1,000 ug/L or less, and TPH sources of 10,000 ug/L or less are attenuated with 5 feet of clean overlying soil.

NOTE: The sample events that require over 8 feet of clean soil are from sites where the sample intervals are 8-10 feet apart or there is unreported soil contamination or free product. Attenuation at these sites likely occurs in 8 feet or less based on the trend shown by all the other data in the d-base.

Criteria for Evaluating Data Set

- Clean soil overlies groundwater (dissolved sources)
- Known depth to groundwater and dissolved sources
- Groundwater & soil vapor data collected at about same time (concurrent) from close proximity
- Complete attenuation of soil vapors defined by shallow soil vapors = 0 or <DL (which does vary; full attenuation verified by samplers/authors)
- Majority of soil vapor measurements from multi-depth soil vapor points, representative sub-slab events included
- LUST sites AND refineries
- -LNAPL sites evaluated separately

Of these sub-slab (sub-building) events, about 10 each for benzene and TPH are multidepth sub-slab sampling points, which are very helpful for studying the effects of buildings on vapors from underlying sources, and oxygen distribution beneath buildings

Criteria for Evaluating Data Set

- Clean soil overlies groundwater (dissolved sources)

- Known depth to groundwater and dissolved sources

- Groundwater & soil vapor data collected at about same time (concurrent) from close proximity

- Complete attenuation of soil vapors defined by shallow soil vapors = 0 or <DL (which does vary; full attenuation verified by samplers/authors)

- Majority of soil vapor measurements from single-depth soil vapor points
- LUST sites AND refineries
- -LNAPL sites evaluated separately

The field data indicate that coarse-grained soil requires less than 5 feet of clean soil thickness to attenuate vapors associated with 6,000 ug/L benzene. This is opposite of the J&E model predictions because the model assumes less attenuation in sand due to greater air-filled porosity in sand. Field data suggest that coarse-grained soil is more permeable for oxygen as well as contaminants.

The field data indicate that fine-grained soil requires 5 feet of clean soil thickness to attenuate vapors associated with 1,000 ug/L benzene. This is opposite of the J&E model predictions because the model assumes greater attenuation in clay, for example, due to clay's physical properties. Field data suggest that fine-grained soil is less permeable for oxygen as well as contaminants.

Vapor attenuation in hard rock formations is similar to that in coarse-grained soil. 5 feet of rock attenuates vapors associated with dissolved benzene concentrations up to 3,000 ug/L.

Criteria for Evaluating Data Set

- Clean soil overlies groundwater (dissolved sources)
- Known depth to groundwater and dissolved sources
- Groundwater & soil vapor data collected at about same time (concurrent)
- Complete attenuation of soil vapors defined by shallow soil vapors = 0 or <DL (which does vary; full attenuation verified by samplers/authors)
- Majority of soil vapor measurements from multi-depth soil vapor points, representative sub-slab events included
- LUST sites & refineries included
- -LNAPL sites evaluated separately

This plot was derived using a different method of analyzing the d-base (decay-ratebased) and confirms that PHC vapors are degraded most rapidly in coarse-grained soil.

This analysis was conducted by Matt Lahvis by applying R-UNSAT to the soil-gas data contained in R. Davis' database. Matt Lahvis's R-UNSAT Model is available at the United States Geological Survey website:

http://nj.usgs.gov/toxics/models.html#R-UNSAT: "In a calibrative mode, R-UNSAT can be used to estimate rates of mass transport, biodegradation and volatilization rates, or transport properties of unsaturated-zone sediments. In a predictive mode, R-UNSAT can be used to predict the distribution of a species as a function of time and space and to estimate mass-loss or loading rates to ground water." The BioVapor Model can also be used to perform similar analyses.

Matt Lahvis, 2010: "This plot of first-order biodegradation rate vs. soil type shows that the rate decreases for lower-permeability soils where the O2 may be more limited." In other words, coarse-grained soils are most permeable to oxygen, which is necessary for degrading petroleum hydrocarbons.

The Hal's site, introduced in a previous slide, was the subject of a vapor intrusion investigation. LNAPL extends about 300 feet down-gradient of the site and numerous multi-depth soil vapor monitoring wells were installed. This vapor profile shows that vapor concentrations are high at the deep depth (15 feet) and fully attenuated just above the contaminated soil zone at 11 feet. Using this consistent method for evaluating the database for this method for screening approach, the thickness of clean soil is reported as 4 feet. To err on the side of caution, the deep depth, even though it lies within the zone of soil contamination, is necessarily accounted for in the data analysis. The actual thickness of clean soil needed to attenuate vapors may be much thinner.

Past work on vapor attenuation associated with LNAPL sources (Davis RV, 2009) used an overly conservative method by subtracting the deepest SV point where vapors are attenuated from the depth to GW. That method unnecessarily accounts for contaminated soil. The new method, shown in this example, is more realistic and can be used for screening soil-only contaminated sites as well as smear zones associated with LNAPL sites.

The Petroleum Vapor d-base contains a data sub-set that is used for determining the thickness of overlying soil necessary for fully attenuating vapors from their respective LNAPL sources. There are 43 paired benzene SV & GW field measurements from 6 geographic locations; 11 events beneath buildings. Screening criteria emerge showing that benzene vapors associated with LNAPL sources are attenuated with 30 feet of overlying soil. There may be contaminated soil included in this analysis due to LNAPL smear zones that are not reported for all sites in the d-base.

Criteria for Evaluating Data Set

-Data for 3 LUST sites (Chillum, Coachella, Hal's) & 3 refineries (Chatterton, Mission Valley, Refinery Site (unknown location)

-LNAPL sources reported at known depths

-Complete attenuation of soil vapors defined by shallow soil vapors = 0, <DL (which may vary; full attenuation verified by samplers/authors)

- Soil vapor measurements from multi-depth and sub-slab completion points

Past work on vapor attenuation associated with LNAPL sources (Davis RV, 2009) reported that 30 feet of soil attenuate vapors. That method, however, unfairly accounted for some contaminated soil in the total soil column evaluated. The thickness of only clean soil required to attenuate associated vapors is only 8 feet.

In late 2009 and early 2010, further refinement in analyzing the data in the Petroleum Vapor dbase involved determining the thickness of only clean, aerobic soil necessary for attenuating vapors associated with contaminated soil and LNAPL. The thickness shown here are based on known or estimated depth to the top of contaminated soil and therefore known thickness of aerobic soil, the essential medium for degrading petroleum. This thickness was determined by measuring the distance between the shallowest SV point where vapors are clearly present and the deepest SV point where vapors are fully attenuated. That distance represents the thickness of the necessary aerobic zone, which is a maximum of 8 feet.

Most of the data is from LUST sites. There are 3 refineries in the data set: Chatterton, Mission Valley, Refinery Site-unknown U.S. location.

Criteria for Evaluating Data Set

- Known/suspected depths and intervals of uncontaminated soil, top of contaminated soil and LNAPL smear zone, and deep contaminated SV

- Complete attenuation of soil vapors defined by shallow soil vapors = 0, <DL (which may vary; full attenuation verified by samplers/authors)

It is important to have a clear decision pathway and set of procedures to ensure consistency and avoid unnecessary work. Utah's LUST program follows 6 basic steps to determine if the PVI pathway may be complete. Utah's procedures are based on the EPA OSWER Draft VI Guide, which is the only available current federal guidance.

Screening Criteria PVI Pathway Not Complete

Dissolved Sources

✓ 5 feet CLEAN soil overlying Benzene ≤1,000 ug/L, TPH ≤10,000 ug/L

LNAPL Sources

✓ 8 feet CLEAN soil overlying top of LNAPL smear zone

 \checkmark 30 feet TOTAL soil for less-characterized sites

Soil Sources (See California updated draft LUFT Manual, July 2010)

 \checkmark 5 feet CLEAN soil overlying TPH <100 mg/kg, PID <10 ppm-v, O2 >4%

Soil Vapor Sources

 \checkmark Vapors are attenuated below the receptor

The Petroleum Vapor d-base has abundant information on the behavior and fate of subsurface petroleum hydrocarbons that can be used to apply screening criteria in order to protect human health and the environment and limited financial resources. These opinions are my own and I hope this information is helpful for states and other entities that are developing or re-thinking their own screening criteria for the vapor intrusion pathway.

THANK YOU

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